

THE EFFECTS OF SYNTHESIS PH AND HYDROTHERMAL TREATMENT ON THE FORMATION OF ZINC ALUMINIUM HYDROTALCITES

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ABSTRACT

Zn/Al hydrotalcites were synthesised by coprecipitation at increasing pH from 6.0 – 14.0, followed by hydrothermal treatment at 150 °C for 7 days. The materials were characterised by XRD, STEM, ICP-AES, thermal analysis, infrared spectroscopy and Raman spectroscopy. The XRD analysis for the samples prepared between pH 9.0 – 12.0 showed a pattern typical of hydrotalcite, with a c-axis distance of ~22.6 Å. STEM showed that the pH of preparation affected the stability of the hydrotalcite and that instability, observed at pH 9.0, favoured the formation of mixed phases when treated hydrothermally. It was also shown that treatment of a stable starting material increased the crystallinity and resulted in the formation of hexagonal plate shaped particles. ICP-AES and thermal analysis showed that the Zn/Al ratio and thermal stability increased with pH. Thermal analysis showed three major weight losses corresponding to the loss of interparticle water, interlayer water and dehydroxylation of the hydroxide layers and decarbonisation of the interlayer region.

1. Introduction

Anionic clays, such as hydrotalcites, are not as well known and rarer in nature than cationic clays such as smectites. The first hydrotalcite was discovered in Sweden around 1842 [1]. Anionic clays have a structure electrically opposite to that exhibited by cationic clays. Their structure can be derived from the brucite structure, $\text{Mg}(\text{OH})_2$, where each Mg^{2+} ion is octahedrally surrounded by six OH^- ions. The hydrotalcite-type (HT) structure is obtained when some of the Mg^{2+} ions, or other divalent cations, are replaced by trivalent cations, with a similar radius [2]. The higher charge of the trivalent cations imposes an overall positive charge on the brucite-type layer, which is compensated by the incorporation of generally hydrated interlayer anions.

A wide range of compositions are possible for synthetic hydrotalcites, based on the general formula $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{b+}[A^{n-}]_{b/n} \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are the divalent and trivalent cations in the octahedral positions within the hydroxide layers with x normally ranging between 0.17 and 0.33, A^{n-} is an interlayer anion with a negative charge n , b is the charge of the layer and m is the number of water molecules. Many anions or anionic complexes, both organic and inorganic, can and have been incorporated into the hydrotalcite structure. The wide range of materials of this type that can be synthesised gives rise to a range of applications including catalysts and catalyst precursors, ion exchangers and adsorbers, anion scavengers and stabilisers, etc [3, 4].

Several factors are important in the precipitation of HT compounds, such as the nature of the cations, their ratio, the nature of the anions, pH, temperature, aging, and the precipitation method. Although generally anionic clay particles are larger than their counterpart, the cationic clays, there is still interest in the ability to increase particle size, to improve their chemical and physical properties.

A recent study has shown that the carbonate anion concentration in the interlayer region of hydrotalcite was affected by both temperature and aging [5]. It was shown that the best crystalline material was obtained at 25 °C, with at least 5 hours of aging. Generally, it is accepted that a basic pH is required for the preparation of hydrotalcites. However, the optimal pH depends on which cations are used and where their hydroxide precipitation curves cross. The crystallinity of the precipitated hydrotalcite can be further increased by hydrothermal treatment [6, 7]. In 1980 Miyata showed that using a higher temperature, 180 °C, for hydrothermal treatment increased the crystallite size [8]. Several studies have reported on the influence of the synthesis parameters and show that pH is the major factor in the formation of Zn/Al hydrotalcite [9-13]. Zn/Al hydrotalcites have been used for anion exchange reactions, pillaring and absorption [14-24] and a number of catalytic applications, either with the hydrotalcite structure or after calcination as the mixed metal oxide [25-32].

This study forms part of an ongoing investigation on the effects of reaction conditions during synthesis and hydrothermal treatment of the hydrotalcite minerals with various cations and anions to improve their physical and chemical properties. The aim of this study is to obtain insight into the nature of the Zn/Al hydrotalcite-type materials when the experimental conditions are varied. Samples were prepared over a wide pH range, and the reagent addition was optimised. Samples were selected, based on their purity, stability and crystallinity, and treated hydrothermally to investigate 1) the effects of aging under the influence of temperature, pressure and time, and 2) the effects of pH of preparation on the crystallinity of the hydrothermally treated hydrotalcite.

2. Experimental

2.1. Preparation

Zn/Al hydrotalcites were synthesised by the coprecipitation method, based on a theoretical composition of $\text{Zn}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3) \cdot 4\text{H}_2\text{O}$ [33]. Two solutions were prepared, solution 1 contained 2M NaOH and 0.125M Na_2CO_3 , solution 2 contained 0.75M Zn^{2+} [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] along with 0.25M Al^{3+} [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$]. For sample 1, solution 2 was added to solution 1, for sample 2, solution 1 was added to solution 2. The pH was maintained at ~12, for both methods. The best method was established

on the basis of crystallinity and purity. Using the optimum method, the next series of samples were prepared by varying the pH from 6.0-6.5, 9.0, 9.5, 10.0, 10.5, 11.0, 11.5, and >14, and labelled 3-10. In all experiments solutions were added using a peristaltic pump at a rate of 40ml/min, under vigorous stirring. The pH was maintained constant by adding HNO₃ when necessary. When the addition was complete, the mixture was stirred for a further 1.5 hours, during which time the pH was still maintained constant. Two samples were selected based on their purity, stability and crystallinity and were treated hydrothermally at autogenous water vapour pressure at 150°C, in Teflon lined stainless steel Parr Bombs for 7 days (samples 11 and 12). All samples were filtered, thoroughly washed several times, in approximately 500 mL of deionised water each time to remove excess soluble ions, and finally the samples were oven dried at 60°C for 1hr.

2.2. Characterisation

2.2.1. Powder X-ray Diffraction

Powder XRD (XRD) diagrams were recorded on a Phillips wide-angle PW 1050/25 vertical goniometer equipped with a graphic diffracted beam monochromator. The d-values and intensity measurements were improved by application of an in-house developed computer aided divergence slit system enabling constant sampling area irradiation (20mm long) at any angle of incidence. The radiation applied was Co-K α from a long fine-focus Co tube operating at 40kV and 40mA. The samples were measured in the stepscan mode from 5 to 75°2 θ with steps of 0.02°2 θ and a counting time of 2 seconds. Jade software package (Materials Data, Inc.) was used to analyse the data, identification of the existing crystalline phases was based on comparison with pre-existing JCPDS diffraction data files. Pattern manipulation and interpretation was performed using TracesV4 (Diffraction Technology Pty. Ltd.) and Microsoft EXCEL.

2.2.2. Transmission Electron Microscopy

Electron micrographs of the samples were taken by the transmission electron microscopy method (TEM) at 200kV with a Philips CM200 Analytical Scanning TEM instrument, equipped with LaB6 filament, cryo vacuum options, and link thin-window Si EDS detector. Microanalysis of selected samples was carried out in STEM mode using an energy dispersive X-ray spectrometer with Link ISIS system. Samples were prepared by suspension in alcohol (70%) and a small amount was placed on a carbon coated copper grid, prior to use in the TEM.

2.2.3. Inductively Coupled Plasma - Atomic Emission Spectroscopy, ICP-AES

ICP-AES was used for elemental analysis of the Zn and Al ions. A calibration series of standards for determining the relative amounts of Zn and Al, were prepared at 10, 50, 100, and 200 ppm. Small amounts of the samples were accurately weighed and digested in 3 mL of 6M HCl along with 1 mL of 6M HNO₃. The relative amounts of each atom were recorded on Varian Liberty 2000 ICP – AES at wavelengths of 394.40 nm and 213.86 nm for Al and Zn respectively.

2.2.4. Thermal Analysis

Differential thermal analysis (DTA) and Thermal gravimetric analysis (TG) of the samples were recorded on a Setaram 2000 (1992) unit. The samples were measured under a stream of argon (20 ml/hr) at heating rate of 2° per minute, from 30°C to 1000°C at heating rate of 2° per minute. Data manipulation and interpretation was carried out using Microsoft EXCEL.

2.2.5. Fourier Transform Infrared and Raman Spectroscopy

Fourier-transform infrared (FTIR) spectra were recorded using the KBr tablet technique (2 wt% sample) on a Perkin Elmer FT-IR 1000 spectrometer; 64 scans were taken to improve the signal to noise ratio in the range of 400 – 4000 cm^{-1} , the normal resolution was 4 cm^{-1} . The Raman spectra were obtained using a Renishaw 1000 Raman Microscope System, which includes a monochromator, a filter system and a charged-coupled device (CCD) as the detector. Raman spectra were excited on a Spectra-Physics model 127 He/Ne laser (633nm), scanned for 15 seconds for 1000 scans and recorded in the range of 400 – 1800 cm^{-1} and 2800 – 4000 cm^{-1} . Data manipulation, such as baseline adjustment, smoothing and normalising as well as interpretation, was performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA) and Microsoft EXCEL. Band component analysis was undertaken using the Jandel “Peakfit” software package, which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly.

3. Results and Discussion.

3.1. Effect of Reagent Addition

The XRD patterns of all samples are shown in Figure 1. The crystalline components in samples 1 and 2 (pH 12) show some significant differences. Both show a sharp symmetric (003) reflection at low 2θ angles corresponding to a c-axis of $\sim 22.8 \text{ \AA}$. Both spectra also show broad asymmetric peaks at higher angles, which are characteristic of clay minerals possessing a layered structure and are similar to the pattern of natural hydrotalcite [7, 34]. Sample 1 (pH 12) however shows additional peaks that are associated with the second major phase zincite, ZnO, and sodium nitrate, NaNO_3 , as a minor phase. The difference in the crystalline products formed is due to the variation in synthesis conditions, where based on the Zn solubility curves precipitation of ZnO starts at pH ~ 9 [35]. The addition of the hydroxide containing solution to the cations containing solution yielded a hydrotalcite-type material without the ZnO impurity. Proceeding via this pathway is therefore preferred as it progresses under acidic conditions that do not favour the formation of ZnO [35]. Under strong alkaline conditions ZnO species are not soluble and compete with the formation of Zn/Al hydrotalcite.

3.2. The effect of pH of synthesis

The pH of preparation is important in the formation of all hydrotalcite-type materials and the optimum pH depends on the cations used (Fig. 1). Sample 3 (pH 6.0-6.5) displays very weak, broad peaks at higher 2θ values (14.9°) compared to sample 2 (pH 12, 13.6°). The XRD patterns of sample 3 (pH 6.0-6.5) shows that no hydrotalcite structure is formed under acidic synthesis conditions. The broadness of the peaks indicates the sample is poorly crystalline, where the reflections occur at

similar 2 θ values as for brucite, indicating that a low crystalline hydroxide similar to brucite is formed instead of hydrotalcite. Samples prepared within the pH range of 9.0-12.0 (samples 4-9, & 2) show patterns similar to that of natural hydrotalcite [7], with the (003) reflection corresponding to a c-axis of ~ 22.5 Å. The difference between these samples is in the intensity of the (00 l) reflections. As pH increases, from 9.0 to 12.0, the intensity of the reflections increases and the line width decreases, corresponding to an increase in crystallinity. Sample 2 and 9 at pH 12 and 11.5, respectively, have the most intense and sharpest peaks, thus are the most crystalline samples. Sample 10 (pH >14) shows a different structure from the previous samples; it is composed of one major crystalline phase being zincite, ZnO, and a minor phase, sodium nitrate. Based on solubility curves and predominance diagrams for Zn²⁺, at this strong alkaline pH zinc-hydroxy complexes, such as hydrotalcites, become more soluble and ZnO the predominant phase that would be precipitated. It is concluded that the hydrotalcite phase formed at lower pHs during synthesis would redissolve, at this high pH to form zincite [35].

The TEM of sample 5 (pH 9.5) shows large particles, 120 nm across, with a distorted hexagonal shape (Fig 2a). The particle morphology was observed to be regular and homogenous throughout. The electron diffraction pattern appeared very weak and the beam exposure was destructive to the sample. The STEM analysis exhibits a bulk ratio of Zn/Al of ~ 2.1 for a cluster of crystals. This analysis also shows that a small amount of nitrogen is present, however the signal was very weak and the crystalline phase could not be identified in the TEM mode. Sample 9 (pH 11.5) shows large particles of ~ 180 nm across. The particle shape of this sample was almost hexagonal and regular throughout the sample. This sample displayed a ratio of Zn/Al = 2.6.

The TEM of sample 10 (pH >14) is primarily composed of rounded, elongated, flat crystals of submicron size (27 – 58 nm). The particle shape is regular and the diffraction pattern was very strong, indicating a highly crystalline phase (Fig 2b). The STEM analysis showed that Zn and O are the major components, and that Al is only present in a trace amount (1/20). This is in agreement with the XRD that indicated only zincite (ZnO) with a minor trace of sodium nitrate as the crystalline components.

Table 2 summarises the chemical composition derived from the ICP-AES analyses for samples 2, 4-9 (pH 12, 9-11.5), with a precision of $\sim 5\%$. The Zn/Al ratio ranges from 1.89 (sample 3, pH 6-6.5) to 2.25 (sample 9, pH 11.5), and differs from the ratios obtained from STEM as they are bulk ratios. It is apparent that, whilst expecting a theoretical ratio of 3, all samples have a ratio of ~ 2 , which is in accordance with the findings of Velu *et al.* [36] and Roussel *et al.* [37, 38] for Zn/Cr hydrotalcite. It is postulated that the lower ratio observed in both studies is due to preferential crystallisation of Zn-hydrotalcite as $Zn_4Al_2(OH)_{10}(CO_3).xH_2O$, rather than a hydrotalcite with a Zn/Al ratio of 3:1. Previous studies have indicated that the possible formation of hydrotalcites involves the reaction of a solution containing the divalent metal with the trivalent metal hydroxide [13]. This would explain the results obtained with samples 1 and 2 (pH 12). It also would explain the increase in crystallinity with the pH. The pH range between 9.0 – 12.0 is considered to be ideal for the preparation of hydrotalcites, and is a commonly used range for their synthesis.

The DTA/TGA patterns of representative samples are shown in Figure 3. The hydrotalcite samples 5 and 9 (pH 9.5 and 11.5) show similar features in both patterns.

The TGA curve does not exhibit well defined plateaus between the decomposition steps which extend over relatively high temperature ranges. However in light of the DTA pattern two major weight losses can be identified, which is in agreement with the well-known decomposition mechanism of such compounds which predicts two distinctive steps of weight loss [39-41]. The first weight loss occurs around 200 °C and reflects the loss of physically adsorbed (surface) and interlayer water [36, 42, 43]. The loss of surface water begins as soon as heating commences and is completed at ~90 °C, the removal of the interlayer water is finished at ~190 °C. TGA-MS study of Mg/Al-hydrotalcite has shown that up to 200°C water is lost in several steps accumulating in a major loss around 195°C [44]. The decomposition step, starting at ~200 °C is due to the decomposition (dehydroxylation) of the hydroxide layers and to the removal of interlayer anions (carbonate) [44]. The end products of the thermal decomposition have been shown to be metal-oxides as well as mixed-oxide spinel type phases [43, 45]. The patterns of various samples differ with respect to the temperature at which the weight losses occur, such that sample 5 (pH 9.5) occurs at a lower temperature than for sample 9 (pH 11.5). Since stability is dependant on temperature sample 9 appears to be the most stable sample from this series [46]. It is concluded, in comparison with the XRD and TEM results, that the more crystalline samples have the highest thermal stability.

The FT-IR spectra for samples synthesised at various pH conditions are shown in Figure 4, and their assignment in Table 1. With the infrared assignment it has to be kept in mind that most of the OH-groups are (when not at the edges of the crystals) triply coordinated to the di- and trivalent cations [33]. If the various metals in the hydrotalcites (Zn, Al) are distributed at random, it is unlikely than an OH-group is surrounded by three metal cations of the same kind, especially Al₃OH. In most cases one OH-group will be coordinated by the two different metal cations. In the following sections the vibrations will be assigned to the coordination which it most likely resembles, e.g. “Al-OH”. All spectra show a very broad band between 2700 and 3750 cm⁻¹. Band component analysis (Fig. 5) reveals three superimposed peaks at 3025, 3348, and 3468 cm⁻¹. The 3025 cm⁻¹ band is generally interpreted as the CO₃-H₂O bridging mode [7, 47]. The 3348 cm⁻¹ band is ascribed to the H-bonded interlayer H₂O surrounding the anions. The strong band at 3468 cm⁻¹ is assigned to the metal-OH-stretching mode. However, the various metals (Zn, Al) bonded to the OH-group cannot be distinguished between [48].

Within the range of pH synthesis conditions the positions of the infrared bands change up to 50 cm⁻¹ and generally the intensity increases with increasing pH. In addition peaks become sharper with increasing pH. Since increasing intensity corresponds to an increase in the order, the samples prepared at pH 11.5 and 12 are the most crystalline and the sample prepared at pH ~6.5 is the least crystalline. All samples have a weak broad peak centred ~1630 cm⁻¹. This peak is associated with the deformation mode of water (ν₂).

Samples 2, 4-9, and 12 (pH 12, 9-11.5 and hydrothermally treated) show a peak centred ~1400 cm⁻¹ in the infrared spectrum, associated with the presence of CO₃²⁻ species in the interlayer region. Assuming the carbonate species is present as the free ion (D_{3h}) and not specifically involved in any bonds, only three bands should be present in the infrared spectrum, ν₂, ν₃ and ν₄ [49, 50]. Comparison of the spectrum carbonate modes with that of the free ion, discloses a shift to lower wavenumbers,

which is due to the interaction of the carbonate ions with the water molecules in the confined space between the hydroxide layers resulting in loss of freedom, therefore leading to a lowering of the carbonate symmetry to C_{2v} or C_v [48]. The out of plane bending mode (ν_2) and in-plane bending mode (ν_4) are usually found at 874 and 680 cm^{-1} respectively. Close examination of the spectra reveals the activation of the symmetric stretching vibration, ν_1 , as a very weak shoulder band at $\sim 1045 \text{ cm}^{-1}$, which is overlapped by the metal-OH translational modes. The lowering of symmetry is further confirmed by the splitting of the ν_3 mode.

In certain samples the ν_3 antisymmetric stretching mode at $\sim 1400 \text{ cm}^{-1}$ has a sharp peak at high intensity with a broad base at low intensity. Band component analysis of sample 4 prepared at pH 9.0 shows the presence of three overlapping bands: one sharp and two broader bands (Fig. 6a). The broader bands at 1359 cm^{-1} and 1399 cm^{-1} are assigned to the antisymmetric stretching mode (ν_3) of the CO_3^{2-} species. The sharper band at 1384 cm^{-1} is assigned to nitrate, as nitrate always gives a very sharp and intense peak around this frequency. It should be noted that with increasing pH the presence of nitrate is no longer observed. The presence of nitrate in the interlayer region of the hydrotalcite is caused by the fact that metal nitrates were used to synthesise the hydrotalcites. Band component analysis of sample 2 (pH 12) shows only two broad peaks at 1361 cm^{-1} and 1397 cm^{-1} corresponding to the splitting of antisymmetric stretching mode, ν_3 , of carbonate to ν_3 and ν_{3a} (Fig. 6b). Sample 3 (pH 6-6.5) also show signs of nitrate, however the carbonate antisymmetric stretching mode has shifted. Sample 3 (pH 6-6.5) shows a very weak broad peak at $\sim 1450 \text{ cm}^{-1}$, which is assigned to carbonate and occurs at a higher wavenumber than for the other samples. XRD has already shown that this sample did not contain any crystalline hydrotalcite, which fits well with the shift in the carbonate band in the infrared spectrum. Sample 10 (pH >14) different as it has a very sharp nitrate peak around 1388 cm^{-1} and a very weak, almost indistinguishable carbonate band. Considering that this sample was characterised as be primarily composed of ZnO, these results are consistent, as no carbonate should be present.

Table 1 gives the infrared band positions, of selected samples between 1000 – 400 cm^{-1} and their assignments. Band component analysis (Fig. 7) shows the complexity of the spectrum in this region, where in most cases a number of overlapping bands exist. The assignment of these bands is consistent with the XRD results, where most samples show a mixture of bands including those of “Zn-OH”, “Al-OH”, CO_3^{2-} and NO_3^- . Sample 2 (pH 12) for example clearly shows in this region a pattern typical of hydrotalcite, where it has a broad shoulder at 868 cm^{-1} and strong bands at 553 cm^{-1} and 430 cm^{-1} [51]. Sample 10 shows no “Al-OH” translations modes, as was expected.

The examination of the samples using Raman spectroscopy compliments the infrared study [52]. The hydroxyl-stretching region (3000 – 4000 cm^{-1}) of the spectra is quite broad and very weak. Figure 8 shows the Raman spectra between 350-1600 cm^{-1} of all samples.

The first group of samples 1,2,4-9, and 12 (pH 12, 9-11.5 and hydrothermally treated) display an intense peak centred at $\sim 1064 \text{ cm}^{-1}$, assigned to the ν_1 symmetric stretching mode (A_1') of carbonate and the “Al-OH” translation [49]. The antisymmetric stretching mode (E') ν_3 and in-plane bending mode (E') ν_4 usually lie at 1415 and 680

cm^{-1} respectively, however are eminently weak and are unable to be confidently assigned [53]. Sample 3 has 2 peaks at 1052 and 1077 cm^{-1} , assigned to the nitrate symmetric stretching mode (ν_1) and carbonate symmetric stretching mode respectively. The frequency of the carbonate symmetric stretching mode has shifted to a higher frequency than the free ion, this is due to the lowering of symmetry from the free ion D_{3h} . Sample 10 (pH >14) shows a very weak and broad 1068 cm^{-1} peak that can not be precisely assigned.

At the lower end of the Raman spectrum, samples that contained an identifiable hydrotalcite phase and exhibited similar carbonate infrared active stretching modes (samples 1, 2, 4-9, 12), also have comparable bands in the Raman spectra. The samples show a peak at $\sim 553 \text{ cm}^{-1}$ assigned to the “Al-OH” translation mode as well as a peak $\sim 500 \text{ cm}^{-1}$ that can be assigned to “Zn-OH” or “Al-OH” translation modes but is probably a combination of both. Both these peaks have shoulders that are too weak to accurately assign. Sample 3 shows no assignable peaks, consistent with XRD and IR, in this region. Sample 10 (pH >14) shows the same peak at 439 cm^{-1} and is more intense and sharper than the former sample. Furthermore, this sample contains no peaks at $\sim 555 \text{ cm}^{-1}$ assigned to “Al-OH” as expected.

3.3. *The effect of hydrothermal treatment of Zn/Al-Ht*

Two samples from the previous pH series were treated hydrothermally; one synthesised at the high pH with good crystallinity (sample 9, pH 11.5), and one at lower pH with poor crystallinity (sample 5, pH 9.5). Figure 1 shows that the two hydrothermally treated samples (11 and 12) have different structures. Sample 11 appears to have lost all of the hydrotalcite structure and is composed of one major crystalline phase, ZnO, and two or even three other minor crystalline phases, containing various amounts of Zn^{2+} , Al^{3+} , CO_3^{2-} , and OH^- . The minor phases are associated with the reflections at 15.0 and 22.6 $^\circ 2\theta$, indicating a small amount of hydrozincite, $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ and/or zinc carbonate hydroxide hydrate, $\text{Zn}_4\text{CO}_3(\text{OH})_6 \cdot x\text{H}_2\text{O}$. The reaction mechanism that plays a major role in the decomposition of the low crystallinity hydrotalcite is unclear at this stage. Sample 12 yielded a highly crystalline hydrotalcite-type compound, where the peaks are more intense and sharper than the sample from which it was prepared. However, there are several small peaks, which are just resolved that are associated with sodium nitrate.

The TEM of sample 11 (Fig 2c) shows numerous crystalline phases. The most obvious phase is thick, needle-like and the largest crystal type in this sample. The type is extremely crystalline, exhibiting a strong electron diffraction pattern, and according to the STEM is primarily composed of Zn and O. This phase is assigned to the hydrozincite, even though carbon could not be observed, but the structure is different from the zincite phase of sample 10 (pH .14). The next phase is structurally similar to the other zincite phase observed with elongated crystals that are rounded at the top. This phase differs from the first phase in terms of the morphology, it is thinner and edges are rounded, and are composed of Zn and O in a different ratio. This phase is assigned to zincite. The third phase has a hexagonal shape with a particle size of $\sim 77 \text{ nm}$ across. The diffraction pattern is strong and the STEM analysis revealed a ratio of Zn/Al of ~ 2 . The fourth phase is also highly crystalline according to the diffraction pattern, and particles have cubic-type morphology. The particle size is approximately the same as the hexagonal shaped phase but smaller than the first two phases. This phase is quite common and appears to make up the

bulk of the sample, and is primarily composed of Al/Zn with a ratio of 5/4. This was not expected since the XRD showed no crystalline Al phase was likely to be present. Although this cubic phase makes up the bulk of the sample, the initial two ZnO phases are highly crystalline and exhibit very strong diffraction patterns, which probably suppress the diffraction of the smaller less crystalline phases. The final identifiable phase is a flat flaky structure, which exhibits a diffraction pattern and is also a crystalline phase. The STEM reveals this phase is composed of Zn, Al, C and O in varying compositions, indicating a hydrotalcite-like phase.

The TEM of sample 12 (Fig 2d) showed large, flat particles (260 nm) similar to those of the untreated samples. Although the morphology of most particles is fairly regular there does appear to be another phase. The predominant phase has a distorted hexagonal shape where some of the edges are rounded, similar to sample 9, indicating signs of dissolution during the hydrothermal treatment. The electron diffraction pattern shows a stronger pattern than sample 9. The STEM analysis found a ratio of Zn/Al ratio of 2.5-3.2, compared to an initial ratio of 2.6 in sample 9. The TEM also showed smaller crystals with a cubic morphology, on the rounded surfaces of larger hexagonal-like crystals, which were too small for microanalyses. Thus hydrothermal treatment increases the crystallinity and allows time for the classical hexagonal shape of the hydrotalcite to form [2, 54]. The presence of the smaller cubic shaped particles indicates that with aging predominant crystal growth occurs on the edges resulting in relatively thin hexagonal plate shaped crystals with rounded edges. These smaller particles are believed the initial stages of growth of a second phase that was found to be present. This second phase consisted of rounded elongated crystals that are composed of Zn and O, in a ratio of 1:1. It is concluded that these particle grew as a result of the dissolution of the larger hexagonal shaped, crystalline phases. However the contribution from this phase to the total sample is small as only a few crystals were observed.

The TGA/DTA of sample 12 is shown in Figure 3. This sample exhibit similar thermal properties as the two starting samples previously discussed. The primary difference between all these samples is the thermal stability. Samples 12 is the most thermally stable, where all decomposition steps occur at higher temperatures than for the other samples. Furthermore this samples confirms that the more crystalline samples are the most thermally stable.

The infrared spectrum of sample 11 is eminently different from the hydrotalcite samples (Fig. 4, Table 1). At high frequency (3000 – 4000 cm^{-1}) a broad feature exists that is assigned to OH-stretching modes. At mid frequency several bands are prominent that are assigned to the presence of carbonate. Band component analysis of this region shows the CO_3^{2-} antisymmetric stretching modes are less superimposed, occurring at frequencies of 1423 and 1510 cm^{-1} . These bands occur at different frequencies as they are not residing in the interlayer, as with the hydrotalcites. Instead it is assumed that carbonate is present in a covalent metal-to-anion bond, Zn-CO_3 , where the individual sites occupied by Zn, C and O have symmetries $C_{3i} = S_6$, D_3 , and C_2 respectively [20, 24]. It is also noticed that they occur at higher frequencies, thus the carbonate species present in this sample is symmetric than those in the hydrotalcites. The band at 1384 cm^{-1} is associated with the presence of nitrate. Furthermore this samples shows another weak, broad, shoulder peak at 1359 cm^{-1} which can be assigned to a vibrational mode of hydrozincite, usually found at 1340

cm^{-1} , which is consistent with previous studies [51]. At lower frequency sample 11 shows a different pattern compared to all other samples. Band component analysis reveals numerous overlapping bands, where the predominant bands are associated with “ZnOH” translational modes (Table 1). Unlike sample 10 ($\text{pH} > 14$), also primarily composed of ZnO, this sample shows CO_3^{2-} and NO_3^- in plane and out-of-plane bends (ν_4 and ν_2), that are associated with the hydrozincite phase, which lie at higher wavenumbers than for the hydrotalcites.

The infrared spectrum of samples 12 (Fig 4) is very similar to those of the other hydrotalcites, although there are several weak bands at low frequency that the other hydrotalcites do not show; these bands lie at a frequency associated with nitrate, 834 and 690 cm^{-1} . The primary difference between the spectra of this hydrothermal samples and the untreated samples is in the intensity; such that sample 12 has more intense, sharper and better-resolved peaks than its starting material, sample 9 ($\text{pH} 11.5$), and all other untreated hydrotalcites. This sample has experienced an increase in crystallinity, with treatment [2, 54].

The Raman spectrum of sample 11 (Fig. 3) shows an intense, broad peak at 1280 cm^{-1} with a shoulder at 1466 cm^{-1} . In this sample the carbonate is not present as the free ion. The position of the band is at higher wavenumber than the other hydrotalcite samples, thus this peak is assigned to a carbonate species with a lower symmetry than the other samples and the free ion. The band component analysis of this region, shows four bands at 1222, 1265, 1319, and 1458 cm^{-1} . These bands are associated with carbonate symmetric and antisymmetric stretching modes, ν_1 and ν_3 . The peaks at 1265 and 1319 cm^{-1} are the ν_1 symmetric stretching modes and 1222 and 1468 cm^{-1} are the ν_3 antisymmetric stretching modes. The antisymmetric stretching modes are assigned to the weaker, broader peaks, as typically these modes are difficult to assign in the Raman spectrum [53]. This sample has another small peak at 1058 cm^{-1} that is assigned to the nitrate symmetric stretching mode, ν_1 . At the lower end of the spectrum, this sample shows the same “Zn-OH” translational peak at 438 cm^{-1} , however no identifiable “Al-OH” peak, as it is probably too weak. Sample 12 shows similar features to the other hydrotalcites, however is more ordered as the peaks are more intense and sharper.

3. Conclusion

XRD, STEM, ICP-AES, thermal analysis, infrared and Raman spectroscopy are powerful methods employed in the characterisation of hydrotalcite – type materials [2]. The effect of reagent addition on the purity and crystallinity of the hydrotalcite materials showed that by adding the base (NaOH) to the acid, proceeding via an acidic pathway, favours the formation of the hydrotalcite. Under strong alkaline conditions ZnO species are not soluble and are found to compete with the formation of Zn/Al hydrotalcites.

The variation of pH showed that at low pH no hydrotalcite-type structure formed and that with increasing pH, up to $\text{pH} \sim 12$, the crystallinity also increased. However, at high alkaline pH (14) ZnO forms, probably from the redissolution of the hydrotalcite materials formed at lower pH. Furthermore the stability of these compounds was observed to increase with increasing pH.

Comparing hydrothermal samples showed that treatment of unstable, confirmed by STEM and thermal analysis, hydrotalcites favours the formation of ZnO and other non-hydrotalcite phases. Where stable starting materials produces highly crystalline hydrotalcite-type products, which maintain the classical hexagonal shaped particle.

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Table 1. Chemical composition of Zn/Al for samples 2, 4-9 with increasing synthesis pH.

Sample	ICP-AES analysis		Sample mass In 200mL (g)	Concentration Ratio Zn/Al
	Al (ppm)	Zn (ppm)		
4 (pH 9)	17.47	80.40	0.0509	1.89
5 (pH 9.5)	15.75	81.03	0.0523	2.11
6 (pH 10)	14.44	74.73	0.0490	2.13
7 (pH 10.5)	16.01	81.95	0.0516	2.11
8 (pH 11)	14.04	73.49	0.0487	2.14
9 (pH 11.5)	16.87	83.92	0.0485	2.16
2 (pH 12)	14.76	80.47	0.0498	2.25

Table 2. Infrared frequencies and assignments of the various modes of vibrations between 1000-400 cm⁻¹ [48, 49, 51].

1 (pH 12)	2 (pH 12)	10 (pH >14)	11 (HT)	12 (HT)	NO ₃ ⁻	CO ₃ ²⁻	Natural HT	Gibbsite [Al(OH) ₃]	Hydrozincite [Zn ₅ (CO ₃) ₂ (OH) ₆]	Zincite [ZnO]	Suggested Assignment
950	942			948				958			“Al-OH” deformation
908			883						900-880		“Zn-OH” deformation
			868			879-866					$\nu_2 - \text{CO}_3^{2-}$
870	868			866			865				$\nu_2 - \text{CO}_3^{2-}$ in a HT
839			833	834	839						$\nu_2 - \text{NO}_3^-$
791	785			793				800			“Al-OH” translation
747	739							749			“Al-OH” translation
			732						738		“Zn-OH” translation
695			690	690	692						$\nu_4 - \text{NO}_3^-$
	686			676		680	670				$\nu_4 - \text{CO}_3^{2-}$
			644						710		“Zn-OH” translation
619	620	617		614						615	“Zn-OH” translation
579	591			587				585			“Al-OH” translation
552	552			553			555	562-540			“Al-OH” translation
		545	557							535	“Zn-OH” translation
518	523	515		521				515	520		“Zn-OH” or “Al-OH” translation
		488	483						460		“Zn-OH” translation
450		440	430							440	“Zn-OH” translation
426	430			435			412	420			“Al-OH” translation
		422									Unknown

FIGURE CAPTIONS

- Figure 1 XRD patterns of all synthetically prepared Zn-Al hydrotalcite samples (1-12) in comparison with each other.
- Figure 2 TEM images of Zn/Al hydrotalcites; (a) sample 5, (b) sample 10, (c) hydrothermally treated sample 11 and (d) hydrothermally treated sample 12.
- Figure 3 Thermal analysis of Zn/Al hydrotalcite of sample 5, 9, 11, and 12; a) TGA, b) DTA.
- Figure 4 FT-IR spectra of all synthetically prepared samples (1-12), showing the effects of pH and hydrothermal treatment.
- Figure 5 Band Component Analysis of the OH-stretching region for the infrared spectrum, of synthetic Zn/Al hydrotalcite sample 2.
- Figure 6 Band Component Analysis of the CO_3^{2-} antisymmetric stretching mode (ν_3) in the infrared spectrum of synthetic Zn/Al hydrotalcite samples (a) 4, (b) 2, and (c) 11.
- Figure 7 Band Component Analysis of the lower frequency region, between 1000-400 cm^{-1} , of the infrared spectrum of synthetic Zn/Al hydrotalcite sample 2.
- Figure 8 Raman spectra of samples, showing these changes brought about by pH and hydrothermal treatment.

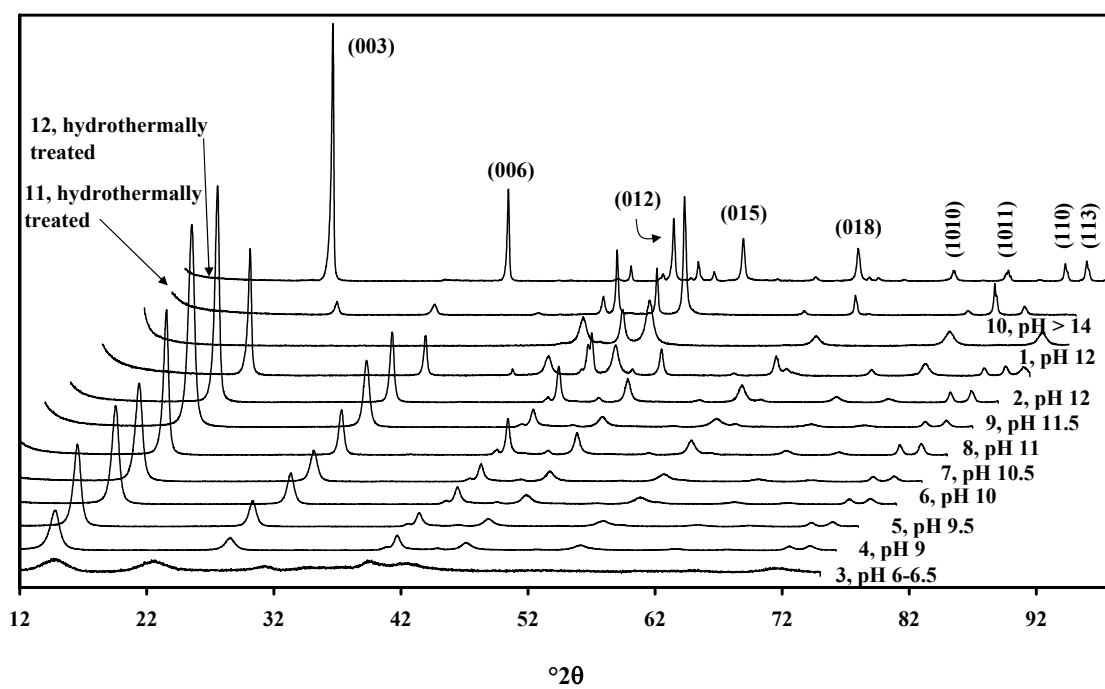


Fig. 1

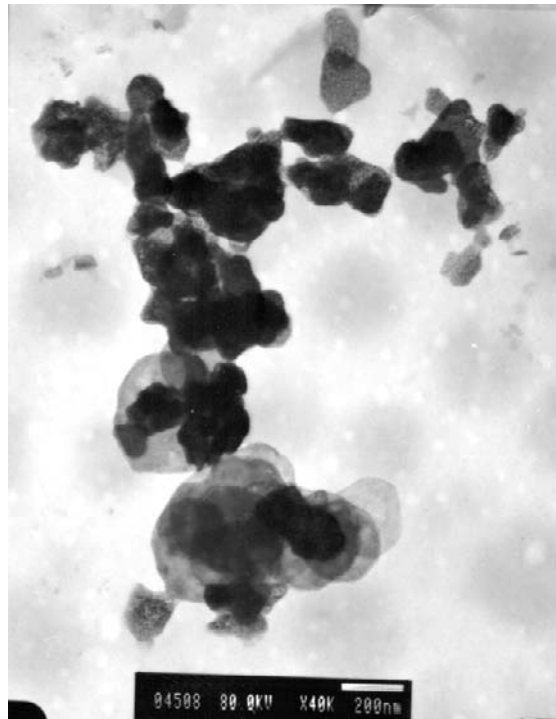


Fig. 2a

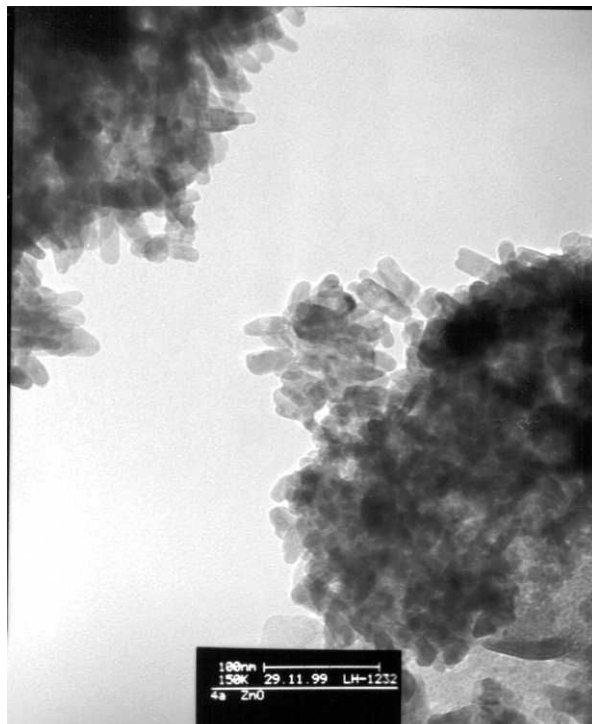


Fig. 2b

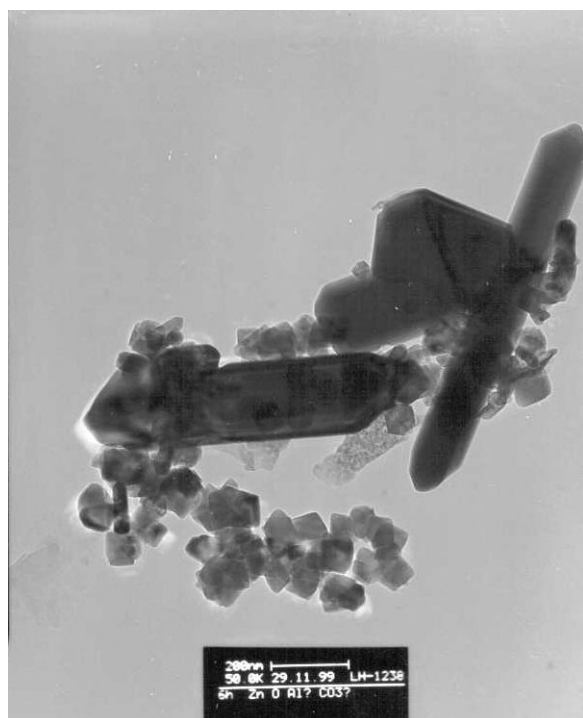


Fig. 2c

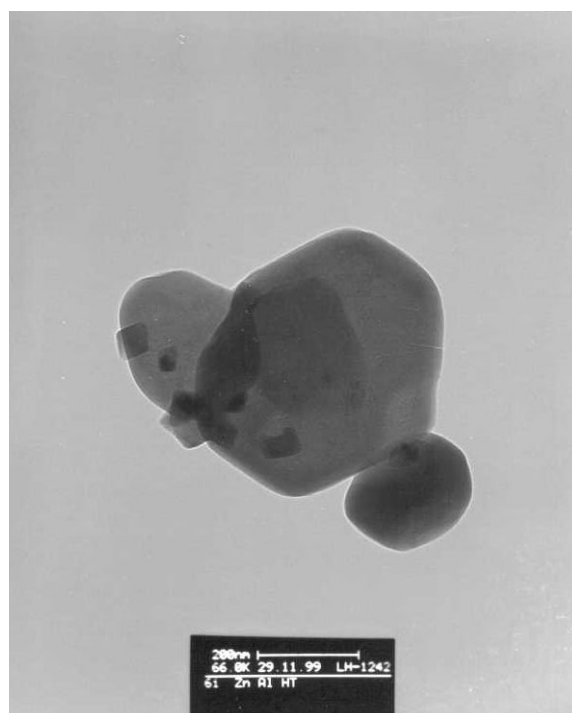


Fig. 2d

FIGURE 2

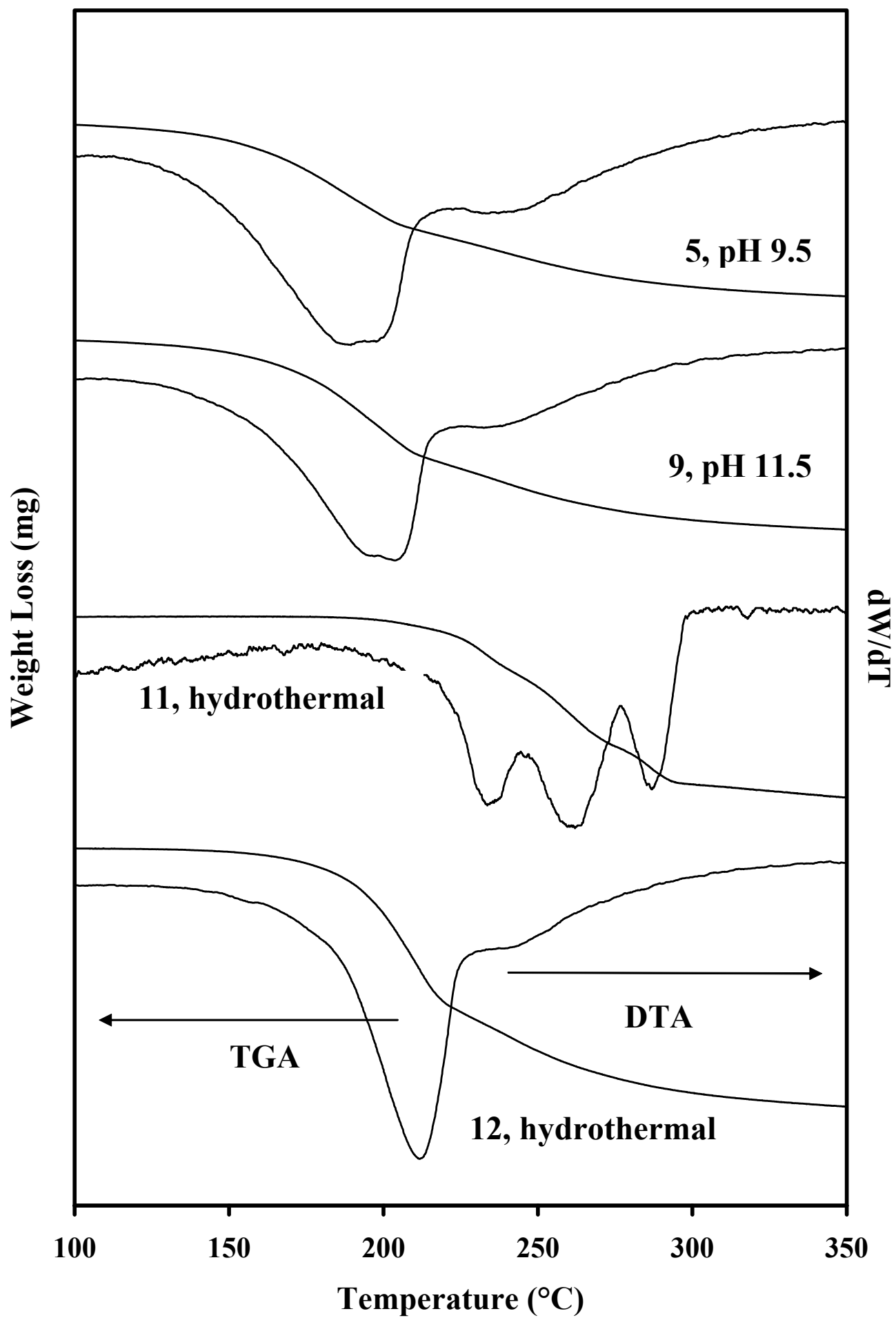


Fig. 3.

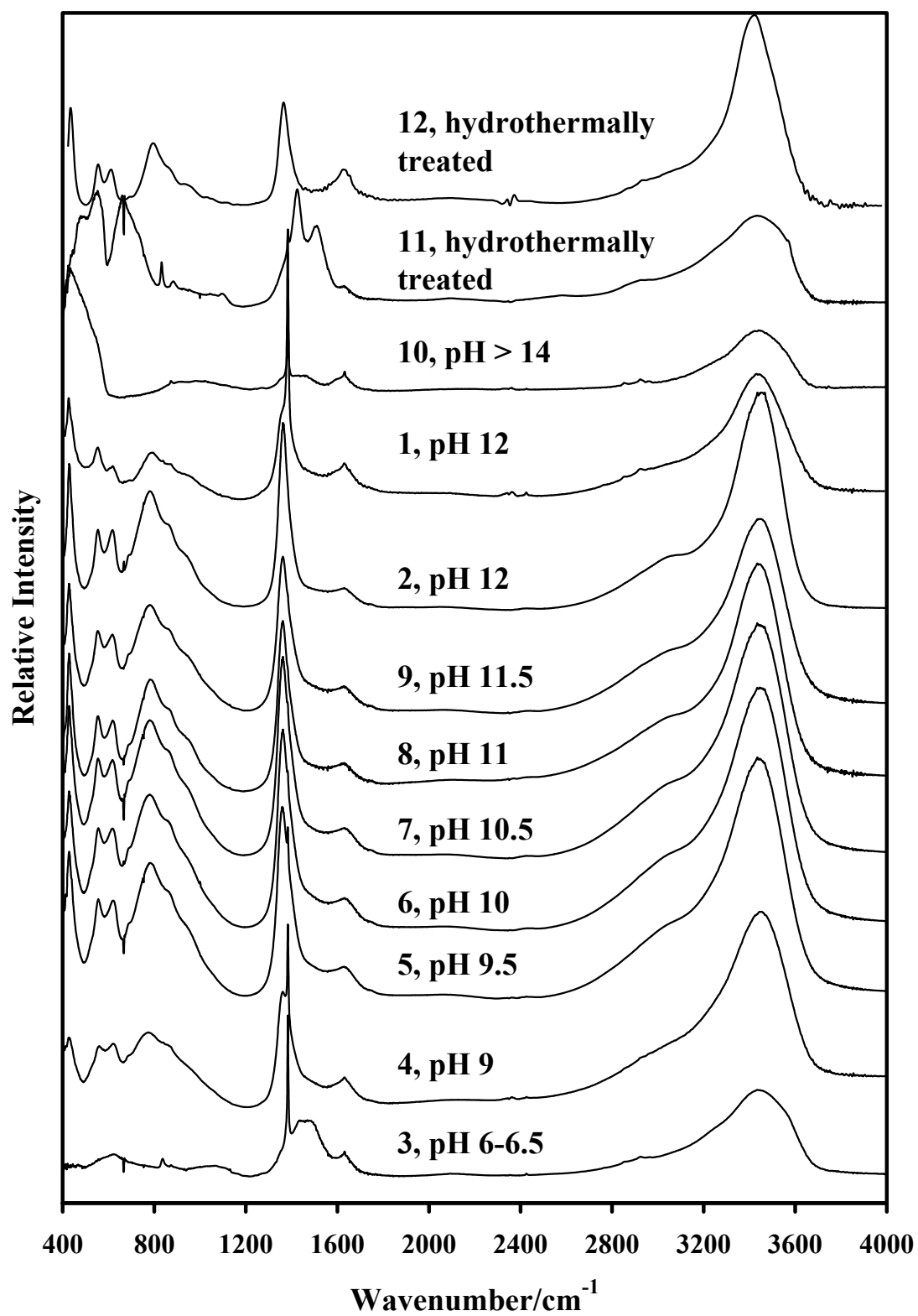


Fig. 4

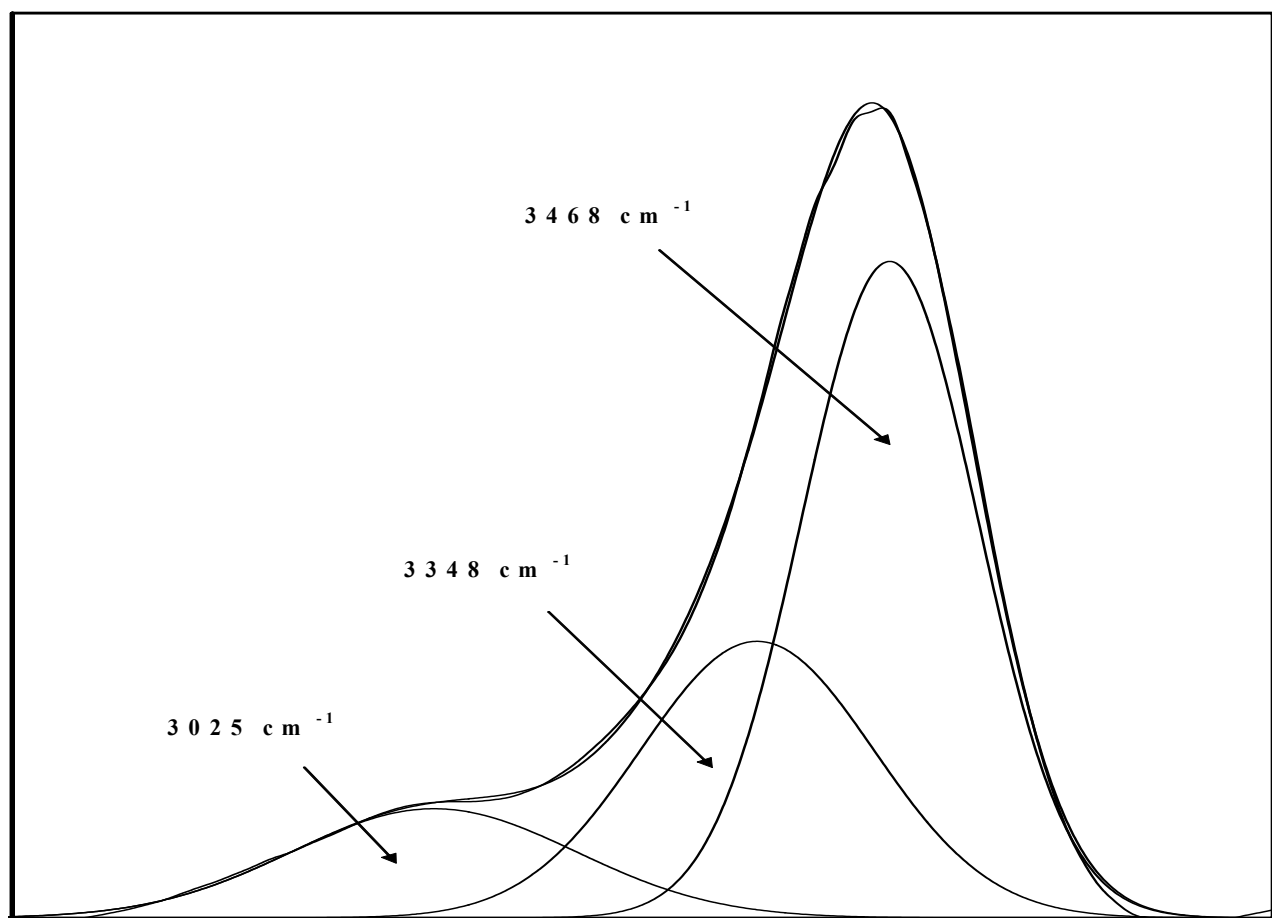
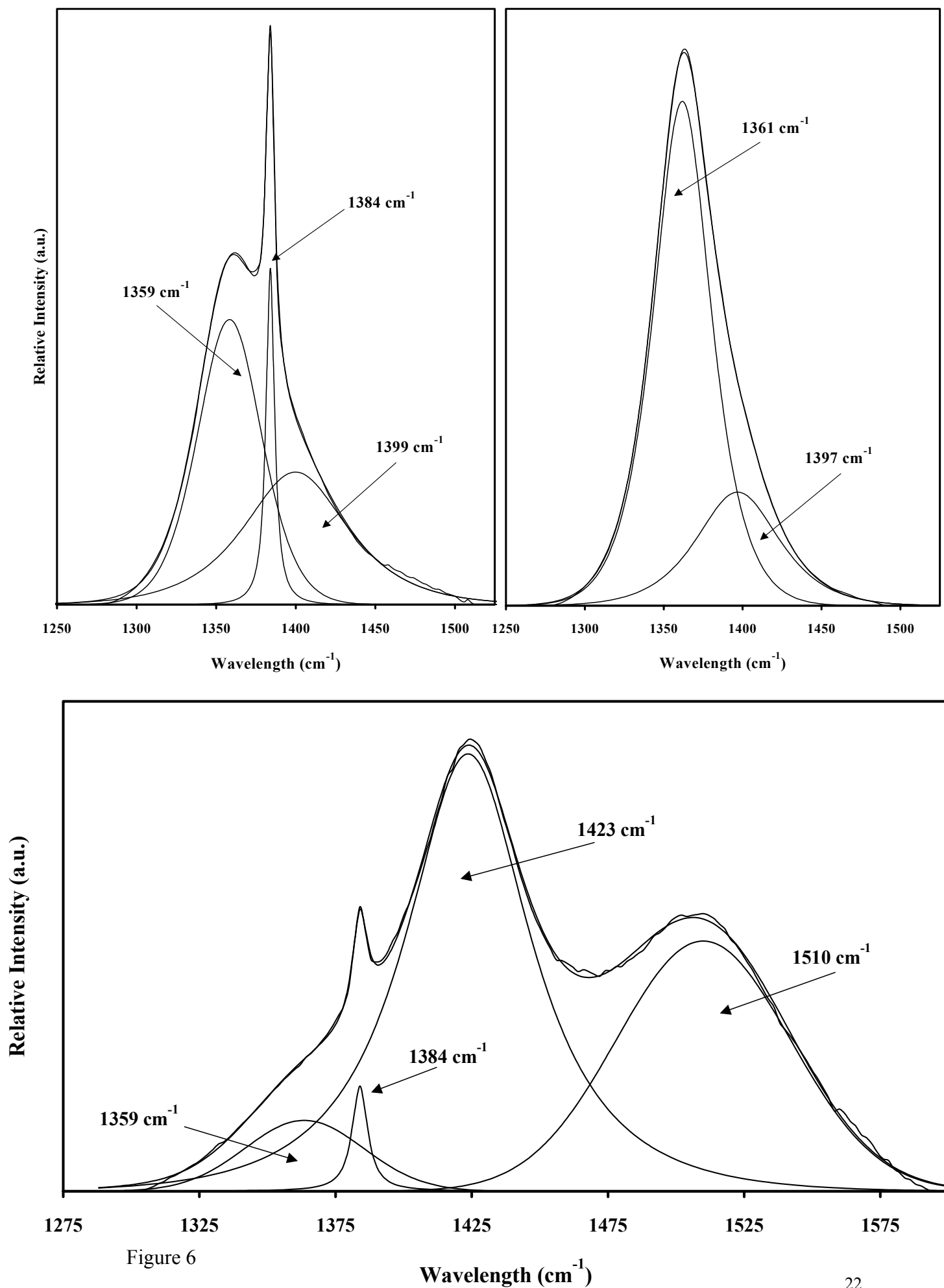


Fig 5



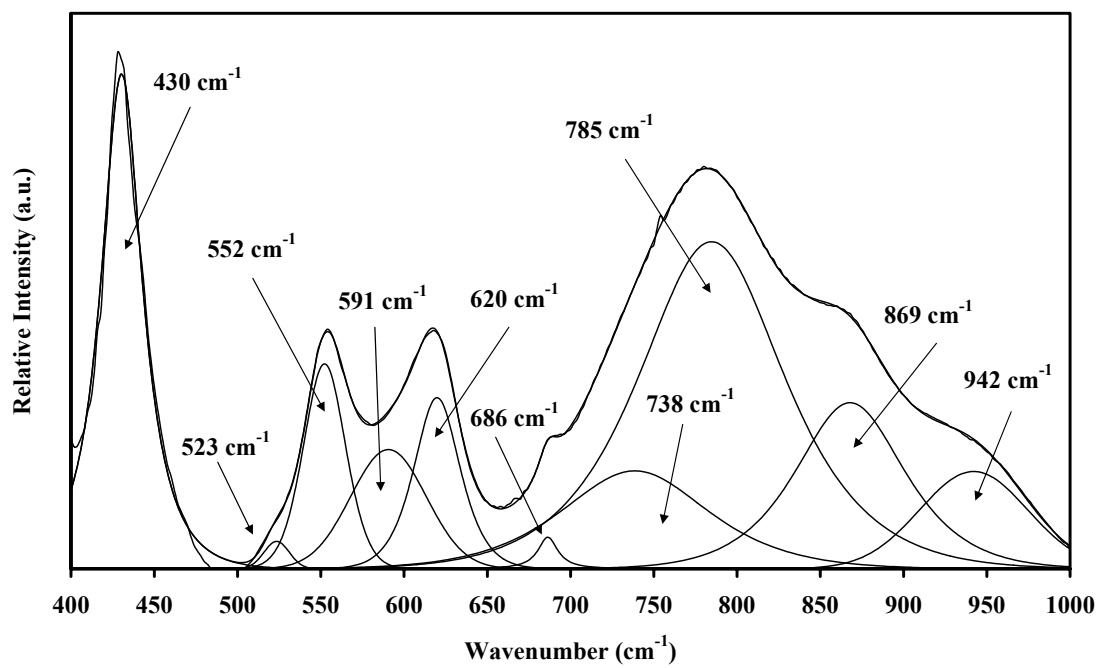


Fig. 7

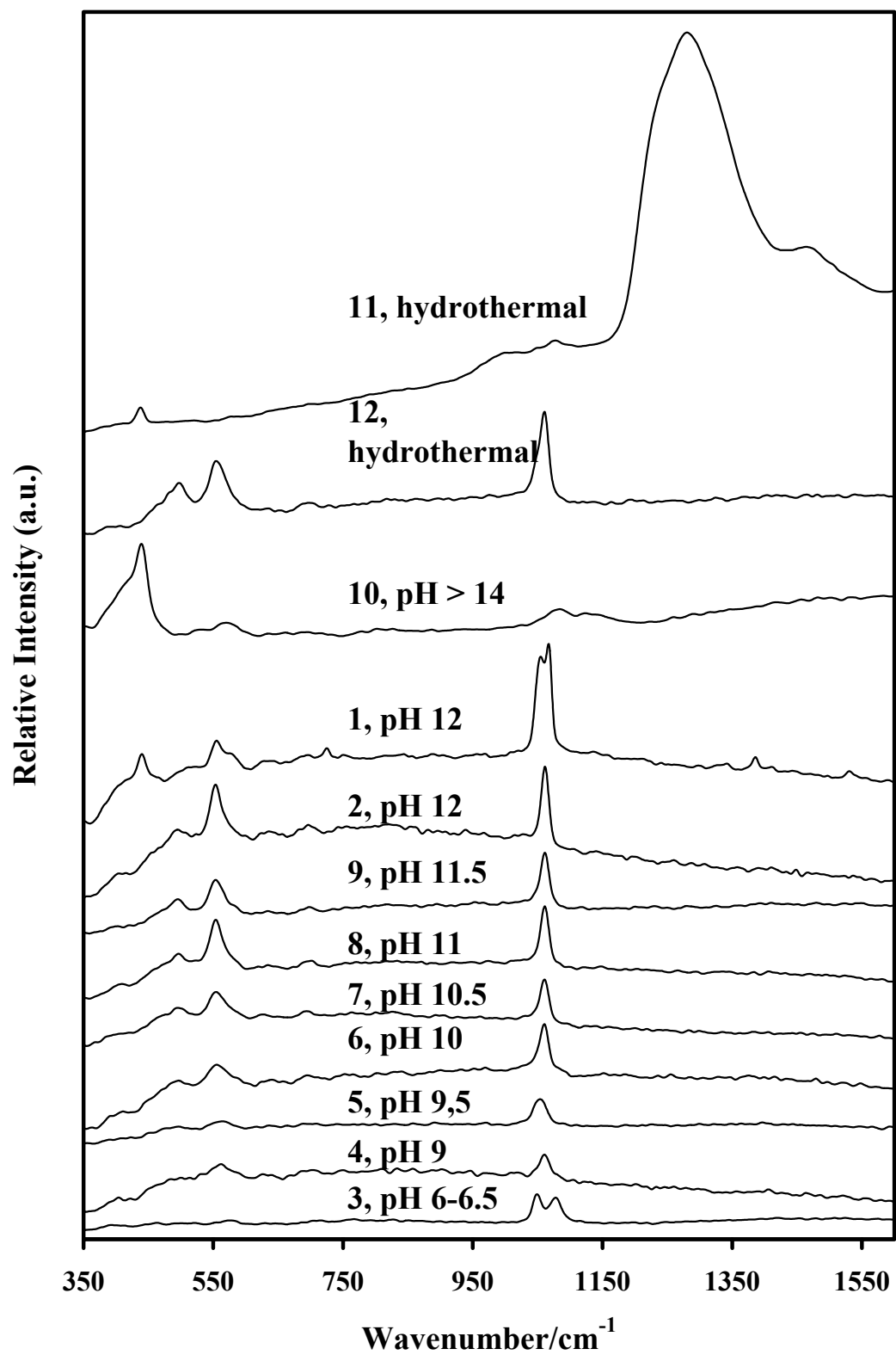


Fig. 8